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THE EFFECT OF RESIDUAL STRESS ON PERFORMANCE OF HIGH TEMPERATURE COATINGS

final report to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546

prepared by

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CONTRACT NO. NASW-2255

NOVEMBER 8, 1972

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THE EFFECT OF RESIDUAL STRESS ON PERFORMANCE
OF HIGH TEMPERATURE COATINGS

I. INTRODUCTION

The purpose of this program was to develop techniques for measurement of residual stress in MoSi_2 coatings and to apply these techniques to the determination of stress in coatings prepared by metallizing, pack and slurry processes.

Under NASW-1403 and NASW-1887, we showed that pest failure in MoSi_2 and C_3Al_2 is basically due to concentration of residual tensile stresses at the tips of Griffith flaws, and resultant localized accelerated oxidation. The effects of residual tensile stress in coatings are by no means confined to pest failure. In fact, the limiting factor in controlling the lifetime of most protective coating systems seems to be the occurrence of random stress-related defects in the form of cracks and fissures. It is thus important that simple, reliable methods be available for evaluating residual stresses in coatings, and further, that tolerance levels of residual stress be developed for particular coatings in specific applications. In the present program, it was expected that measurement methods and tolerance levels would be developed for MoSi_2 coatings.

II. METHODS FOR MEASUREMENT OF RESIDUAL STRESS

Residual stresses between a coating and its substrate result from two principal sources -- conditions during the coating process and differing thermal expansion coefficients when the ambient temperature is changed.

The stress level can be determined by stress induced deflections or by X-ray techniques. The deflection method is most direct. It is based on the fact that a thin substrate, coated on one side only, is usually curved at room temperature. The radius of curvature is easily measured and readily related to residual stress. In the X-ray method, the shift of diffraction lines is measured. The theory relating the

X-ray results to residual stress is well developed and also easy to apply. In the present program, the majority of stress measurements were made by measuring the curvature of a thin strip. The X-ray technique was used to corroborate some of the results on thin strips.

A. Radius of Curvature Method

From a literature review, it is apparent that the curvature method is the favored method for analysis of residual stress in coated materials. It has been used to measure the stress of plated deposits,⁽¹⁾ and stresses generated during oxidation⁽²⁾. The basic analysis of the technique was done by Brenner and Senderoff⁽³⁾. These authors revised original calculations by Stoney⁽⁴⁾ and provided detailed analyses applicable to several specific experimental methods. The analyses of particular interest in terms of our program deal with:

1. Curvature induced when a coating is formed on a rigidly held strip and the constraints of the strip are then released
2. Curvature induced when a coating is formed with no external constraints

The first analysis applied to determination of residual stress resulting from the coating process. The second analysis will be used to calculate residual stress resulting from oxidation.

1. Residual Stress Resulting from Coating. To determine the residual stress produced by siliciding, two thin strips of TZM molybdenum alloy were placed back to back in a double "picture frame" of molybdenum. The thin strips were 0.060 inch thick, 4 inches long and 1/2 inch wide. Dimensions of the picture frame are shown in Figure 1. A groove 1/32 inch wide by 0.016 inch deep was made around the opening of each frame so that the specimen backs were flush with the surface of the holder and would butt tightly to each after assembling the holder. A photograph of the picture frame and specimens is shown in Figure 2. It can be seen from this photograph that six clamps made from molybdenum rod hold the frames together.

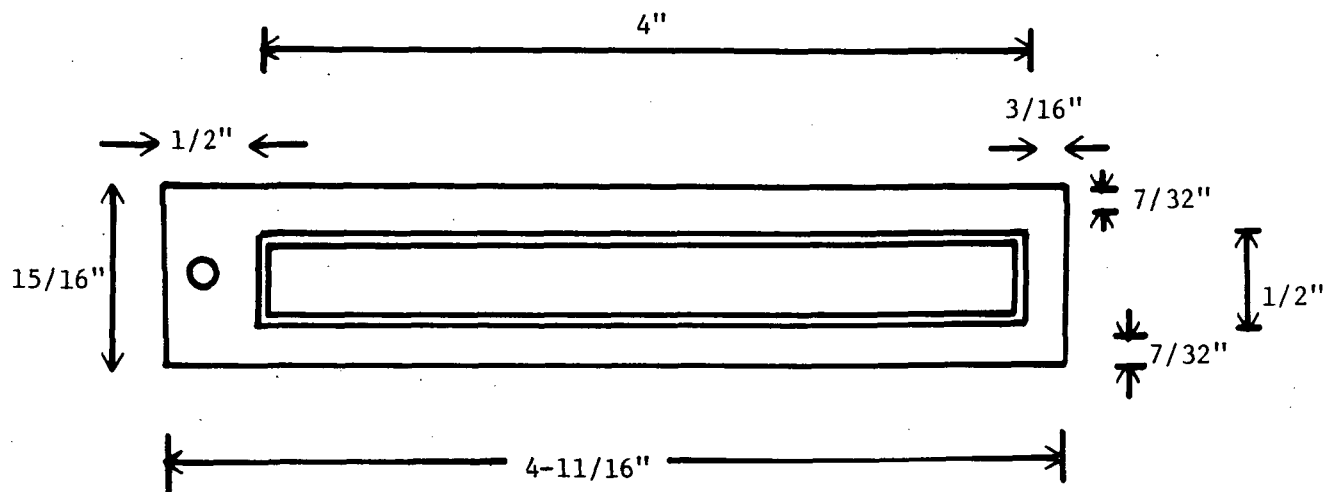


Figure 1. Dimensions of Half Section of TZM Holder Thickness is 0.060"
 Groove around periphery of center cut-out is 1/32" wide and
 0.016" deep

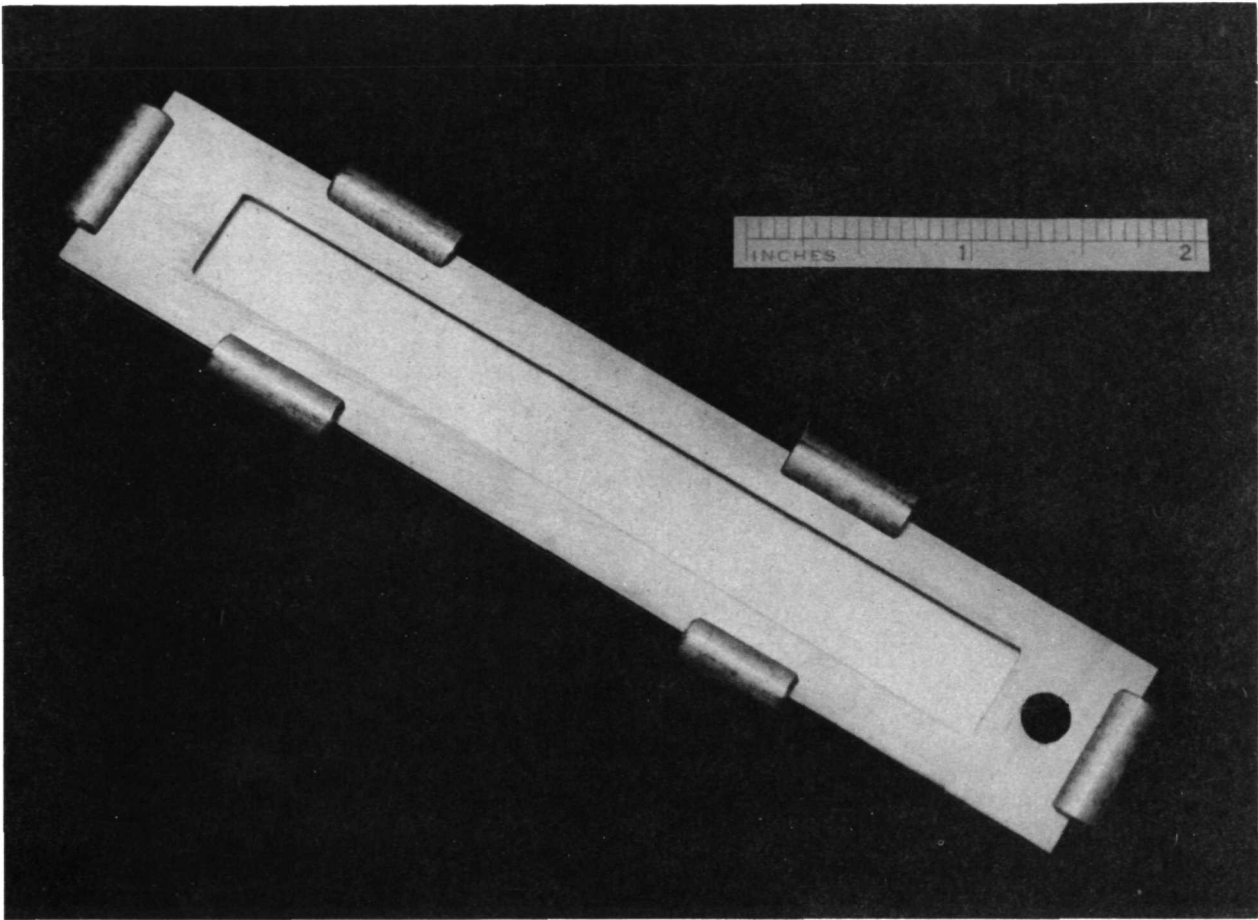


FIGURE 2 TZM SPECIMEN IN FRAME PRIOR TO COATING

After the silicide coating had been applied, the frames were opened and the residual stress determined from the curvature. It is important to distinguish the stress existing before opening up the frame, σ_o , from that existing after the specimen assumes its equilibrium curvature, σ_i :

$$\sigma_o = \frac{4E(t + d)^3 x}{3tdL^2} \quad (1)$$

$$\sigma_i = \frac{4E(t^2 - td + d^2)x}{3dL^2} \quad (2)$$

where E = Young's Modulus of substrate, 45×10^6 psi

t = substrate thickness which is 0.016 inch

d = coating thickness

L = length of the strip which is 4 inches

x = perpendicular distance from the cord to the arc at the midpoint of the cord, i.e., the sagitta of the arc

As an example, the calculations show that for an added-on coating thickness of 0.001 inch

$$\sigma_o = 1.15 \times 10^3 x \text{ where } x \text{ is in mils (0.001 inch)}$$

$\sigma \text{ is in psi}$

$$\sigma_i = 0.90 \times 10^3 x$$

Therefore, 1 mil deflection corresponds to about 1 ksi stress in the coating.

The relaxed stress, σ_i , is about 78% of the unrelaxed stress, σ_o . The latter stress is that which would be determined by X-ray diffraction analysis of a bulk sample while the former is that existing in the coating before oxidation.

The sign of the stress is determined from the sense of the curvature. If the coated side is convex, the coating stress is compressive; and if the coated side is concave, the coating stress is tensile.

For the analysis to apply, the substrate must not yield plastically during bending. From Brenner and Senderoff⁽³⁾ the maximum stress in the TZM molybdenum substrate is given by

$$\sigma_s = \frac{d(4t^2 - td + d^2)\sigma_o}{(t + d)^3} \quad (3)$$

For a 0.016 inch thick substrate with a 0.001 inch thick coating

$$\sigma_s \approx \frac{\sigma_o}{5}$$

The yield stress of TZM exceeds 80,000 psi from room temperature to 1800°F. Thus, the stress in the coating would have to be greater than 400,000 psi for the substrate to yield over this temperature range, and it is unlikely that the coating stress would reach this value.

2. Residual Stress Resulting from Oxidation. During the oxidation experiments the foils were free to bend under the changes in stress, and the stress at the oxidation temperature was calculated from the observed curvature. If the oxide is a mechanically adherent coating, Method III of Brenner and Senderoff (case 2 above) would be used to calculate the stress. Each new layer of oxide affects the stress in the layer of coating below the oxide. If the oxide is not adherent, the stress calculations can be made assuming the gradual removal of the MoSi₂ coating by oxidation.

B. X-Ray Measurement of Residual Stress

Nondestructive measurement of residual stress can conveniently be carried out by X-ray diffraction methods which give the elastic strain normal to the specimen surface. The interplanar spacing of a selected set of diffraction planes is accurately measured at two angles of incidence to determine the elastic strain that is present. Residual stress is then calculated according to the formula:

$$\sigma = \frac{d_{\psi} - d_{\perp}}{d_{\perp}} \cdot \frac{E}{1 + \nu} \cdot \frac{1}{\sin^2 \psi} \quad (4)$$

where

- E = Young's Modulus
- ν = Poisson's constant
- d_{ψ} = interplanar spacing of planes at angle ψ with respect to surface
- d_{\perp} = interplanar spacing of planes parallel to surface ($\psi = 0^{\circ}$)
- σ = stress in surface

To a close approximation, Eq. (4) is given by:

$$\sigma = K (2\theta_{\perp} - 2\theta_{\psi}) \quad (5)$$

where K, the proportionality constant, is called the stress factor and 2θ is the X-ray diffraction angle.

In order to minimize systematic and geometrical errors, one generally employs a high angle reflection ($2\theta = 140$ to 180°) and a value of ψ between 45 and 60° ; the collected data are corrected for differential absorption between incident and diffracted beams (only necessary when $\psi \neq 0^{\circ}$) and geometrical factors which are dependent on the value of θ .

To assure highest sensitivity, it is desirable to employ the para-focusing feature inherent in an X-ray diffractometer. When $\psi \neq 0^{\circ}$, the specimen-to-detector distance must be shortened by a distance x to achieve para-focusing, where

$$x = R \left(1 - \frac{\cos (\psi + \phi)}{\cos (\psi - \phi)} \right) \quad (6)$$

and R = diffractometer radius

$$\phi = (90^{\circ} - \theta)$$

Finally, to accurately measure peak position, 2θ , data is collected at three points straddling the maximum intensity; after correction for absorption and geometric effects, the data is fitted to a parabolic formula which yields true peak position, i.e.,

$$2\theta(\text{true}) = 2\theta_1 + c [(3a + b) / (2a + 2b)] \quad (7)$$

where

$$a = \tau_1 - \tau_2$$

$$b = \tau_3 - \tau_2$$

τ_1, τ_2, τ_3 = time (in seconds) to collect 100,000 X-ray counts at $2\theta_1, 2\theta_2$, and $2\theta_3$, respectively

$2\theta_1, 2\theta_2, 2\theta_3$ = three points where data is collected

$$c = (2\theta_2 - 2\theta_1)$$

For the case of tetragonal MoSi_2 ($a = 3.20$, $c = 7.85$), the (400) reflection occurs at about $2\theta = 148.2$ when CuK_α radiation is used. Residual stress measurements are made with $\psi = 45^\circ$, $x = 7.5$ cm (for $R = 17$ cm), and primary beam divergence is limited to $1/2^\circ$. Assuming values of $E = 45 \times 10^6$ psi and $\nu = 0.25$, and for an accuracy in measurement of 2θ of 0.005° , one can measure the residual stress of MoSi_2 to an accuracy of ± 900 psi.

III. EXPERIMENTAL

A. Coating Application

1. Preparation of Samples. The alloy used for the experiments was TZM molybdenum purchased from the Climax Molybdenum Company in the stress relieved condition. For consistency, foils were cut so that the long axis of the sample was parallel to the rolling direction of the sheet. After machining the foils and holders, the assembled holders with contained foils (Figure 2) were stress relieved to remove machining stresses. The stress relief was done at 2000°F for 5 hours in an

atmosphere of 5% hydrogen-95% argon. Holders were placed in the cold furnace heated to the desired temperature then cooled down to room temperature before removing from the furnace.

2. Metalliding. Siliciding using the General Electric Company's metalliding process was done at Arthur D. Little, Inc. When the proposal was written, it had been intended to have samples metallided by an outside vendor. Although there were several companies, including G. E. active in siliciding at that time, none proved to be in a position to prepare silicided samples on a contract basis now. Since the General Electric Company has reported that silicide coatings formed by the metalliding process are more resistant to peeling than pack or slurry coatings, it seemed important to include metallided coatings in this program. For this reason, the decision was made to set up a cell for siliciding at ADL. Although ADL has had considerable experience with boriding, yttriding, berylliding, and chromiding, siliciding had not been done previously, and a several-month learning period was required before adequate samples were obtained.

Siliciding is done in a molten salt bath having silicon as the anode and the specimen as the cathode of an electrolytic cell. The rate of deposition of silicon is such that silicon diffuses into the substrate to form MoSi_2 but does not plate out. Parameters which can be varied are temperature of deposition, current density and time.

The salt bath charge was 7 lbs LiF , 15.5 lbs KF and 2.5 lbs NaF . Before starting the cell 150 gms of Na_2SiF_6 were added to the salts to build up their silicon content. The cell anode consisted of silicon lumps of 99.999% purity held in a silver wire basket. Operating temperature of the cell was 675°C , the temperature recommended by the General Electric Company to obtain the hexagonal crystal structure of MoSi_2 . Before siliciding the samples in their holders, a number of nickel and molybdenum plates were run to clean impurities from the cell. Many clean up runs had to be made before the weight gains became equal to those expected for the deposition conditions used. Only then could the cell be considered free of impurities.

The optimum metallizing conditions for producing uniform coatings of MoSi_2 on TZM vary with the coating thickness desired. For a 1 mil thick coating, the conditions used were 0.065 amps/in^2 current density for 2 hours. The conditions for a 2 mil coating were first 0.065 amps/in^2 for 2 hours, followed by 0.033 amps/in^2 for 4 hours. It was found necessary to decrease the current density during the later stages of coating to prevent plating.

3. Pack Coating. Pack coating of MoSi_2 onto TZM molybdenum was done by the Solar Division of the International Harvester Company, under the direction of Mr. A. R. Stetson.

one mil coating: 1 hour at 2050°F

two mil coating: 4 hours at 2050°F

Ten specimens, coated to one mil in thickness, were ordered and used in the work described below.

4. Slurry Coating. Slurry coatings of MoSi_2 were prepared by the Sylvania Division of General Telephone and Electronics, under the direction of Mr. Barry Reznik.

B. Characterization of Coated Foils

After the foils were coated in their holders, the residual stress was measured and several foils examined by X-ray diffraction and metallography.

1. X-Ray Diffraction. Both the protected and unprotected faces of the foils were examined by X-ray diffraction. The following phases were found:

Metallized

Coated side	Strong peaks - hexagonal MoSi_2 Weak peaks - molybdenum
Protected (back) side	Strong peaks - molybdenum Very weak peaks - Mo_2C

Pack

Coated side	Strong peaks - tetragonal MoSi_2 Weak peaks - silicon
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Protected (back) side Strong peaks - molybdenum
Weak peaks - Mo_3Si
Very weak peaks - MoSi_2

In agreement with results reported by General Electric, the crystal structure of MoSi_2 is hexagonal as formed in the metallizing process at 675°C . The high temperature tetragonal silicide is formed in the pack process.

The results also indicate that the holders are fairly effective in preventing siliciding on the back sides of each foil which were ostensibly protected. Specimens coated by the pack process did show Mo_3Si peaks on the protected side. These were of much lower intensity than the MoSi_2 peaks on the unprotected side.

2. Metallography. After coating, the foils were examined by optical metallography. In preparation for metallographic sectioning, the foils were electroplated with nickel in order to protect the coating during cutting and polishing. The foils were cut transverse to the face along the width of the foil. After a final polish with 6 micron diamond dust, the specimens were etched in a mixture of 50% ammonium hydroxide and 50% hydrogen peroxide (30% solution) to enhance the contrast between coating and substrate.

Figure 3 shows the structure of a nominal 1 mil coating as prepared by the Solar pack process. The gray areas at the top and bottom of the photomicrograph are the nickel electroplate. The dark band below the nickel is a void due to separation which has occurred between nickel and coating. Metallographically, the coating is uniform and occurs on only one face of the molybdenum substrate. Measured coating thickness is about 0.8 to 0.9 mils. This value agrees with that predicted from the weight gain of 5.2 mg/cm^2 .

A nominal 1 mil coating prepared by metallizing is shown in Figure 4. It is not as uniform as that made by pack process. The average thickness is in the neighborhood of 0.5 to 0.8 mil. The coating is seen to have been formed on one face of the specimen only. No coating is visible on the protected face.

MoSi₂

TZM

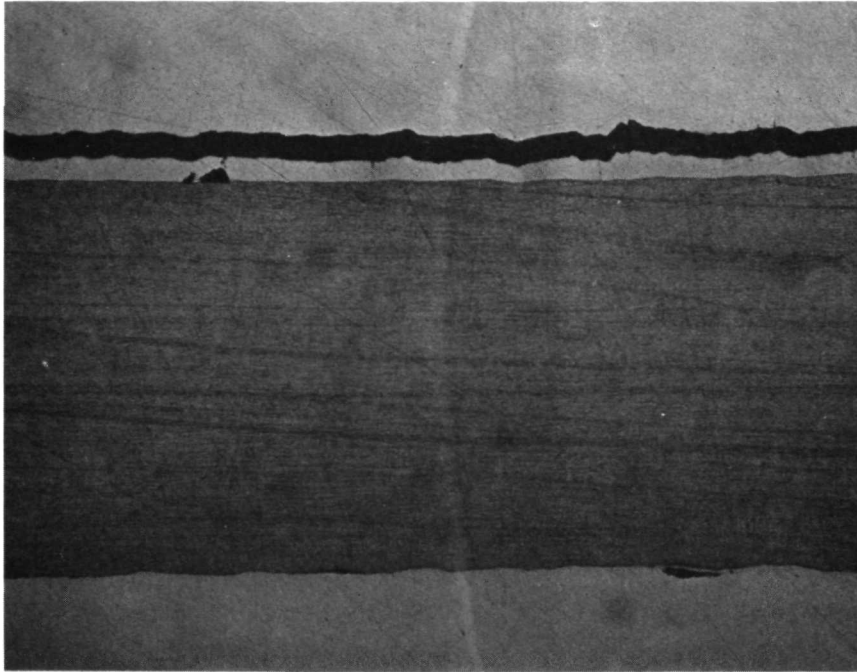


FIGURE 3 PHOTOMICROGRAPH OF MoSi₂ COATING PREPARED BY
THE PACK PROCESS (SOLAR) MAGNIFICATION 125X

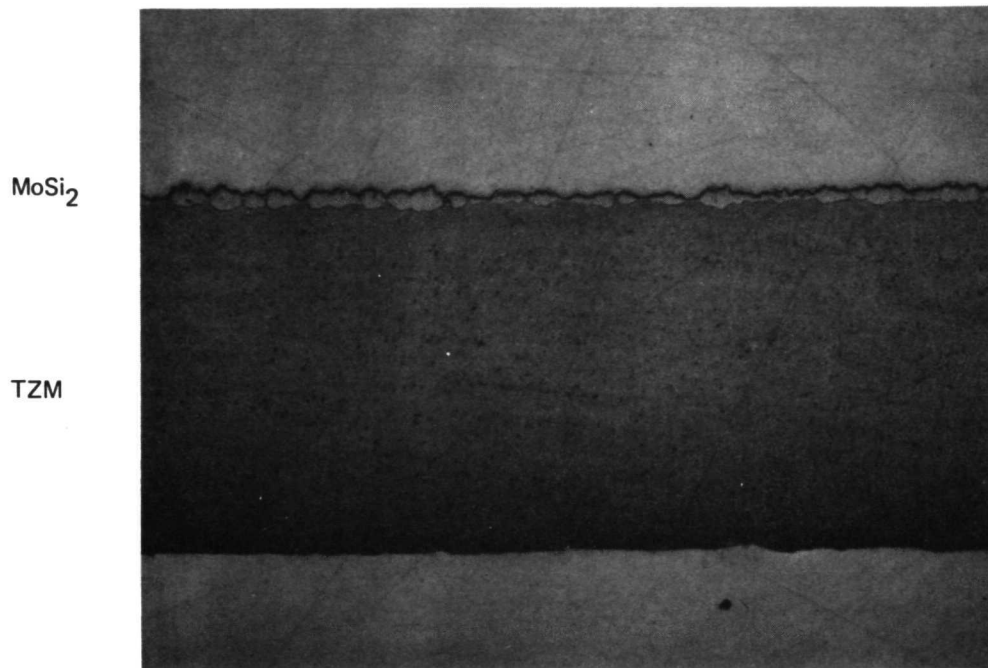


FIGURE 4 PHOTOMICROGRAPH OF MoSi_2 COATING PREPARED BY
THE METALLIDE PROCESS (ADL) MAGNIFICATION 125X

C. Stress Measurements

After removal from the holders the stress in the samples was determined by the radius of curvature method. Measurements were made of the sagitta of the arc using a toolmaker's microscope. As a reference the sample was placed against a 1/2 inch deep steel-parallel.

Stress measurements show that the metallized coatings have a compression stress, σ_o , of about 50,000 psi. The pack coatings have a tensile stress of 30,000 psi. X-ray stress measurements on two of the pack coatings yielded tensile stresses of 41,000 and 61,000 psi, respectively. Since the curvature method is more direct and has been tested more extensively, it was used throughout the remainder of the program to establish trends. Further work would be required to determine why there is a difference between the X-ray and radius of curvature methods of stress measurement. It should be expected that the coating formed by the pack process would be in tension since the thermal expansion coefficient of tetragonal MoSi_2 $9 \times 10^{-6}/^\circ\text{C}$ is larger than that of the substrate $6 \times 10^{-6}/^\circ\text{C}$. The reason for the compression stress in the coatings formed by the metallizing process is not known.

IV. OXIDATION EXPERIMENTS

A. Tests

Oxidation of the MoSi_2 coated TZM Sheet was carried out at two temperatures--450°C and 500°C. Although tests were to be run at 650°C, a satisfactory protective coating could not be found for the unsilicided specimen face at this temperature. The specimens were oxidized in air in a muffle furnace. Specimens were weighed and the curvature measured at room temperature after each oxidation period in the muffle furnace.

Even for the lower temperature experiments, the development of a coating to protect the silicide-free surface and edges of the samples from oxidation proved to be a major obstacle which had to be overcome. Various techniques were tried such as electro-deposited chromium, vapor deposited aluminum, vapor deposited platinum and vapor deposited platinum-gold alloy, but these coatings were not sufficiently protective at the

oxidation temperature of 500°C. The only coating which gave protection was a silicone-based aluminum paint, HITEMP. This paint has to be baked out at temperatures of 400°C or greater. In the weight gain data reported the painted specimens were given about a 20 hour baking treatment in air at the oxidizing temperature, and in the test data reported, the accumulated time begins after this treatment.

B. Materials

It was intended that the three coating processes - metallizing, pack and slurry - would yield specimens having three different stress levels. Upon receipt of the specimens, it became apparent that the Solar pack-coated specimens would be the most suitable for experimentation. All of the Solar specimens had coatings which were uniform, adherent and free from macrocracks, whereas only a small portion of the ADL-prepared metallized specimens appeared to have reasonable coatings. The Sylvania prepared slurry coated specimens were not suitable for testing, since the slurry coating had caused the specimens to bond to the holders.

C. Effect of Elevated Temperature on Stress in the Metallized Coatings

In view of the fact that the metallized coating is hexagonal, as opposed to the pack coating which is tetragonal, and also that it is compressive rather than tensile, four metallized specimens were heated in an argon atmosphere to 1000°C for 20 hours. This heat treatment caused the residual stress to change from a compressive to tensile, and transformed the crystal structure to tetragonal. The following table summarizes the results.

<u>Coating Thickness</u>	<u>Stress in Coating Before Elevated Temperature Treatment</u>	<u>Stress in Coating After Elevated Temp. Treatment</u>
1 mil	64,000 psi compression	43,000 psi tension
1 mil	53,000 psi compression	26,000 psi tension
2 mil	39,000 psi compression	28,000 psi tension
2 mil	42,000 psi compression	15,000 psi tension

The heat treated specimens were then compared with as-metallized specimens having the compressive-hexagonal coating to determine if any

difference in oxidation properties exist. The results of these tests are reported in a subsequent section of this report. The phase transformation and the resultant change in sign of the residual stress is clearly important since in most of the proposed service applications the coating would be subjected to temperature in excess of 1000°C for at least part of the life cycle.

D. Imposed Stress

In addition to the oxidation experiments on samples with residual stress in the coating, oxidation tests were also carried out on pack-coated specimens with an imposed stress. Several samples coated by Solar were placed in a jig and bent to an imposed stress of 20,000 psi tension over and above the residual stress.

E. Results of Oxidation Experiments

Plotted in Figure 5 is the result of the tests of the Solar specimens at 500°C. From this figure it may be readily seen that much shorter inflection times were obtained for the two higher stressed specimens than for theunjigged specimens; notably about 50 hours as opposed to 500 hours. Thus the oxidation of the molybdenum disilicide coated specimens in this intermediate temperature range is stress dependent, in accord with results previously obtained on monolithic MoSi_2 samples.

The shape of the curves in Figure 5 closely resembles those obtained for polycrystalline molybdenum disilicide. They are characterized by a brief period of rapid weight gain, an intermediate period when the weight changes little with time, and finally a period of accelerating rate. This inflection time is associated with the overall disintegration of the coating as was the case with polycrystalline molybdenum disilicide.

Plotted in Figure 6 are the results at 450°C. As at 500°C, specimens with a superimposed stress oxidized in much shorter times than unjigged specimens without imposed stress. The principal effect of temperature is that the inflection times are somewhat longer at 450 than 500.

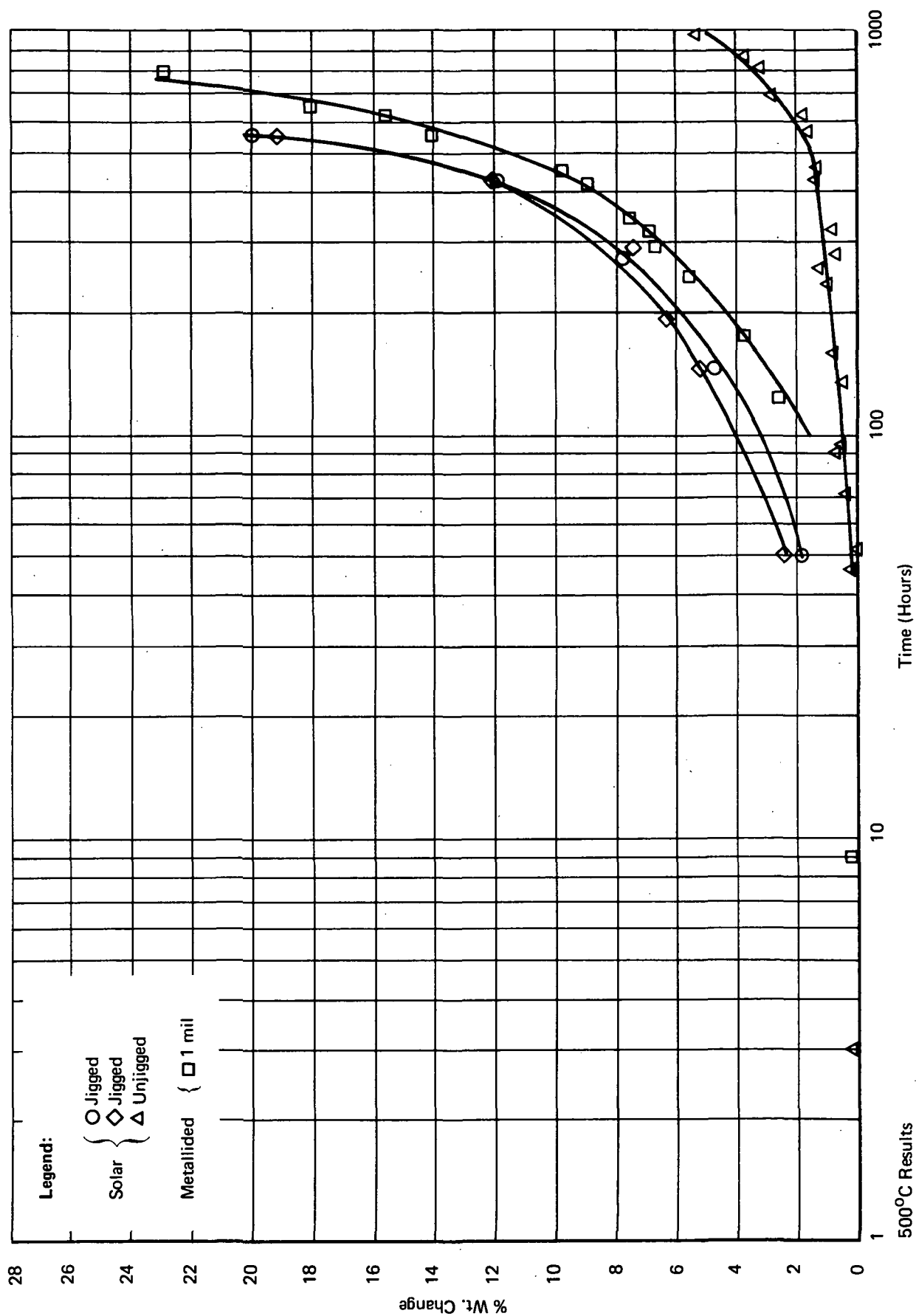


FIGURE 5 PERCENT WEIGHT CHANGE VERSUS TIME — PACK-COATED SILICIDES

In Figures 5 and 6, the results obtained with the metallized specimens for both 500°C and 450°C, respectively, are compared with results for the Solar specimens of the same coating thickness. Because of the lack of quality of these coated specimens, no conclusions have been drawn based upon these data. It was felt that the 1 mil coating did not provide suitable protection but that the 2 mil coating was better and more reproducible. An inflection time of about 80 hours was observed at 500°C, compared to several hundred hours at 450°C.

As shown in Figure 7, change of the residual stress of the metallized coatings from compression to tension had no effect on oxidation rates. Samples which had been heated for 20 hours at 1000°C in argon before oxidation showed the same oxidation rate as those which had not received this pretreatment. It would appear that quality of the metallized coating possibly had more influence on the oxidation rate than residual stress.

As mentioned previously, the change in deflection of the pack-coated specimens was monitored as a function of oxidation time. These results are plotted in figures for 450°C and 500°C runs. From the curves it may be seen that as oxidation progresses, the curvature of the specimen hence the stress level increases. The curvature increase is less at 500°C. This is the temperature of maximum peeling failure and possibly spalling at this temperature reduces the rate of buildup of stress during oxidation.

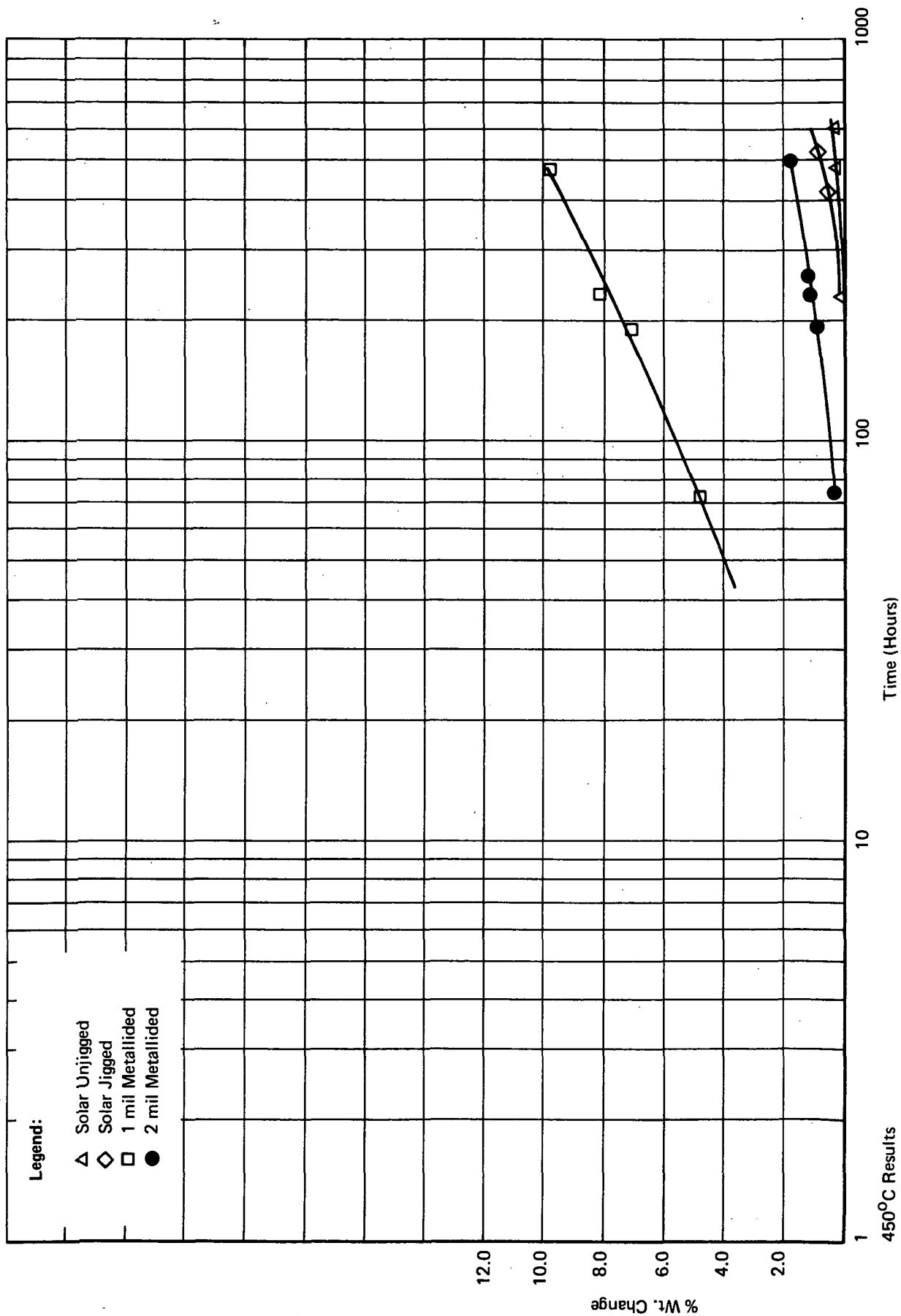


FIGURE 6 PERCENT WEIGHT CHANGE VERSUS TIME — PACK-COATED SILICIDES

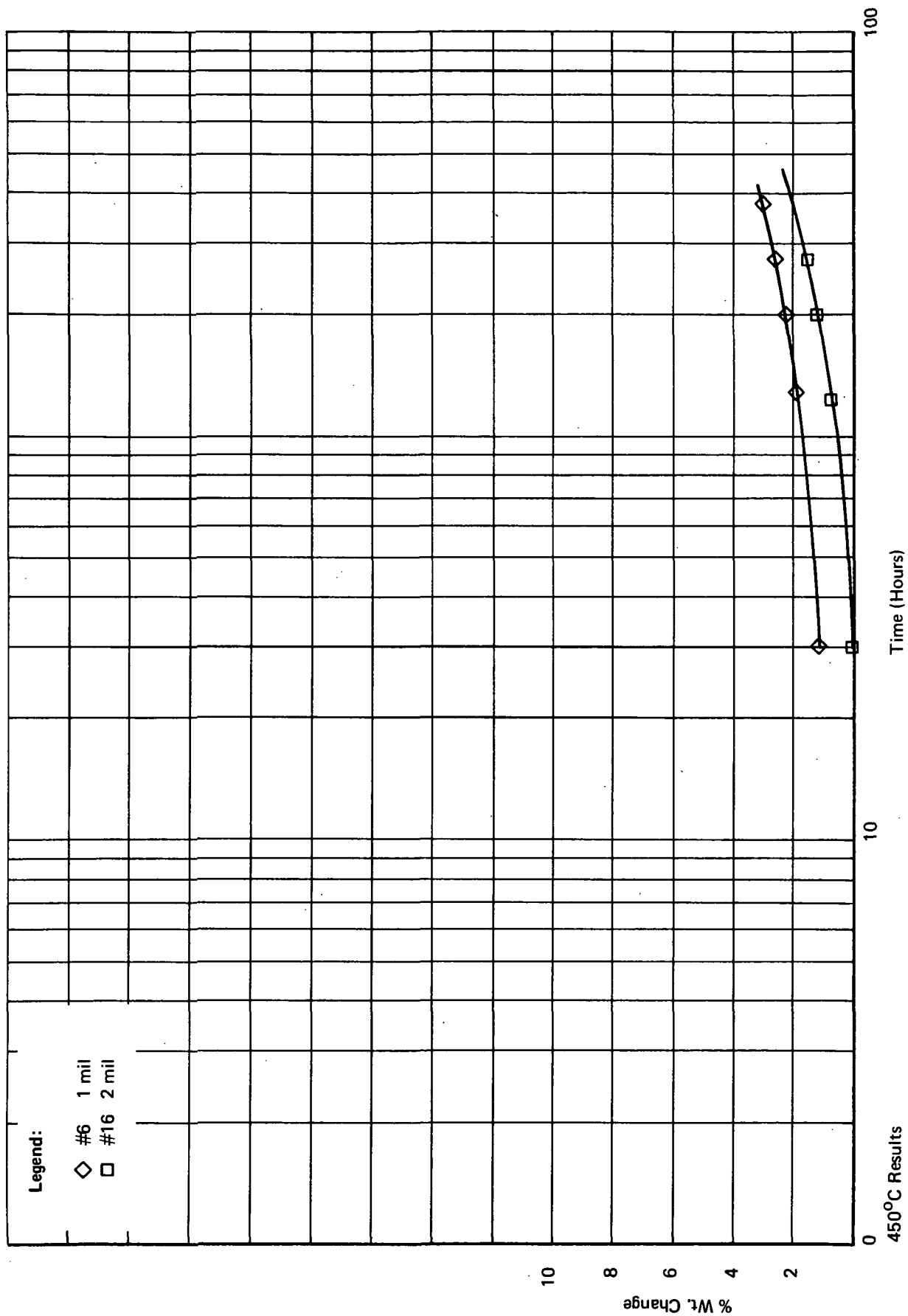


FIGURE 7 PERCENT WEIGHT CHANGE VERSUS TIME — PACK-COATED SILICIDES

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